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# Injection-limited electron current in a methanofullerene

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The dark current of bulk-heterojunction photodiodes consisting of a blend of a methanofullerene (PCBM) as *n*-type electron acceptor and a dialkoxy-(*p*-phenylene vinylene) (OC<sub>1</sub>C<sub>10</sub>-PPV) as *p*-type electron donor sandwiched between electrodes with different work functions has been investigated. With ohmic contacts for hole and electron injection, the dark current appears completely dominated by the electron current in the PCBM, as a result of a much higher electron mobility. This electron current is bulk space-charge limited. With Au as a high work function metal, the electron current becomes injection limited. The injection-limited electron current from the Au electrode into PCBM is explained within a thermally assisted hopping model. In spite of the presence of an injection barrier of about 0.76 eV, the injection-limited electron current from a Au electrode into PCBM still exceeds the bulk-limited hole current in OC<sub>1</sub>C<sub>10</sub>-PPV. © 2003 American Institute of Physics. [DOI: 10.1063/1.1604959]

## I. INTRODUCTION

Conjugated polymer-fullerene bulk-heterojunctions appear to be among the most promising candidates for full organic photovoltaic cells.<sup>1</sup> Such devices consist of a three-dimensional interpenetrating network of the two materials, sandwiched between two electrodes with different work functions to generate an electric field over the active layer. The photovoltaic response is based on an ultrafast excited-state electron transfer from the conjugated polymer as a donor to buckminsterfullerene (C<sub>60</sub>) as acceptor, with quantum efficiency close to unity.<sup>2</sup> A power conversion efficiency of 2.5% under AM1.5 illumination has been obtained for devices consisting of a methanofullerene derivative [(PCBM) [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester] as an electron transporting acceptor and poly [2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene] (OC<sub>1</sub>C<sub>10</sub>-PPV) as the hole transporting electron donor.<sup>3</sup> Following the ultrafast electron transfer, the separated charges are transported via the interpenetrating network to the electrodes and provide voltage for injection into an external circuit. The transport of holes across thin films of pure OC<sub>1</sub>C<sub>10</sub>-PPV has been extensively studied in polymer light-emitting diodes and a hole mobility  $\mu_h$  of  $5 \times 10^{-11}$  m<sup>2</sup>/V s has been obtained at room temperature.<sup>4</sup> Recently, the electron transport in PCBM has been investigated.<sup>5</sup> Occurrence of a space-charge limited current in PCBM has allowed the direct determination of the electron mobility  $\mu_e$  from the *J*-*V* mea-

surements. At room temperature, the electron mobility in PCBM amounts to  $\mu_e = 2 \times 10^{-7}$  m<sup>2</sup>/V s, being almost four orders of magnitude larger than the hole mobility in OC<sub>1</sub>C<sub>10</sub>-PPV. However, the transport of separate charge carriers in an interpenetrating network may be different than the transport in the individual compounds. In the present study, the transport and injection of charge carriers in OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM bulk-heterojunction diodes is investigated and compared to devices with pure OC<sub>1</sub>C<sub>10</sub>-PPV or PCBM layers.

## II. EXPERIMENT

Devices were prepared as follows. The with patterned indium tin oxide (ITO) covered glass substrates were first cleaned by ultrasonic treatment in acetone, rubbing with soap, rinsing with demineralized water, refluxing with *isopropanol*, and finally UV ozone treatment. Subsequently, a layer of PEDOT:PSS (Bayer AG) was spin coated from an aqueous dispersion under ambient conditions on the cleaned substrates and the layer was dried by annealing the substrate. Then the active layer was spin coated on a Chemat Technology spin coater model KW-4A at 1500 rpm from a chlorobenzene solution on top of the PEDOT:PSS layer and the sample was transferred to a N<sub>2</sub> atmosphere glove box. The active layer either consisted of pure OC<sub>1</sub>C<sub>10</sub>-PPV, pure PCBM, or a OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM blend (in a weight ratio of 1:4). As backelectrodes LiF/Al (1 nm/100 nm) or Au (100 nm) were deposited by thermal evaporation under vacuum ( $5 \times 10^{-6}$  mbar, 1 ppm O<sub>2</sub> and <1 ppm H<sub>2</sub>O). Organic film thickness measurements were performed with a

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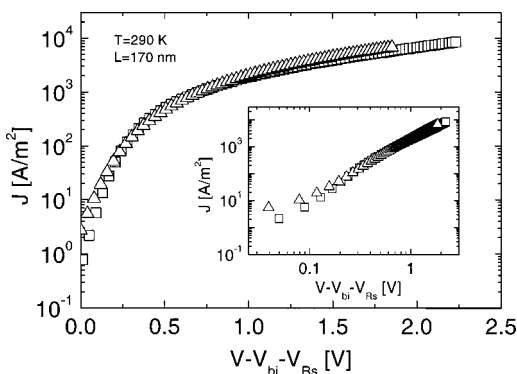


FIG. 1. Experimental  $J$ - $V$  characteristics of an ITO/PEDOT:PSS/OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM (1:4) /LiF/Al diode in the dark (squares), together with a PCBM electron only device (triangles) with a thickness of  $L = 170$  nm at a temperature  $T = 290$  K. The  $J$ - $V$  characteristics are corrected for voltage drop across the ITO serial resistance ( $\sim 11 \Omega$ ) ( $V_{Rs}$ ) and for a built-in voltage ( $V_{bi} = 1.4$  V) that arises from the work function difference between the contacts. The inset shows the same data in a log-log plot to demonstrate that the current density depends quadratically on the voltage, characteristic for SCLC.

Tencor P10 surface profiler.  $J$ - $V$  curves were measured with a Keithley 2400 source meter in an Oxford Optistat continuous flow, exchange gas cryostat.

### III. RESULTS AND DISCUSSION

In Fig. 1 the experimental current density  $J$  of an PEDOT:PSS/OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM (1:4 w/w) /LiF/Al diode with thickness  $L = 170$  nm is shown, together with the electron current density for a 170-nm-thick PEDOT:PSS/PCBM/LiF/Al device. The applied bias  $V$  has been corrected for the built-in voltage ( $V_{bi} = 1.4$  V) that arises from the work function difference between the ITO/PEDOT:PSS and LiF/Al contacts. For large current densities (larger than  $1000 \text{ A/m}^2$ ), the applied voltage has also been corrected for the voltage drop across the ITO series resistance ( $V_{Rs}$ ), which typically is  $11 \Omega$  in our substrates. The slope of the  $\log(J)$ - $\log(V)$  plot (inset of Fig. 1) demonstrates that the current density depends quadratically on the voltage ( $J \propto V^2$ ), consistent with space-charge limited current (SCLC). It appears from Fig. 1 that in forward bias the dark current in OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM (1:4 w/w) bulk-heterojunction diodes is equal to the electron current in pure PCBM. The fact that the experimental  $J$ - $V$  curve of the bulk-heterojunction diode lies on top of the PCBM device indicates that the electron mobility of PCBM in the bulk heterojunction is not significantly affected by the presence of OC<sub>1</sub>C<sub>10</sub>-PPV up to 20 wt %. Furthermore, the SCLC behavior of PCBM demonstrates that the use of LiF/Al does not represent a significant barrier for electron injection.<sup>5</sup>

In order to investigate the hole current in a OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM bulk-heterojunction diode, the electron current needs to be strongly suppressed. As a result of its high work function an Au electrode is expected to form a blocking contact for injection of electrons into PCBM. This approach has been successfully applied in polymer-based light-emitting diodes to make "hole-only" devices.<sup>6</sup> In the inset of Fig. 2 an energy band diagram of such a device is shown

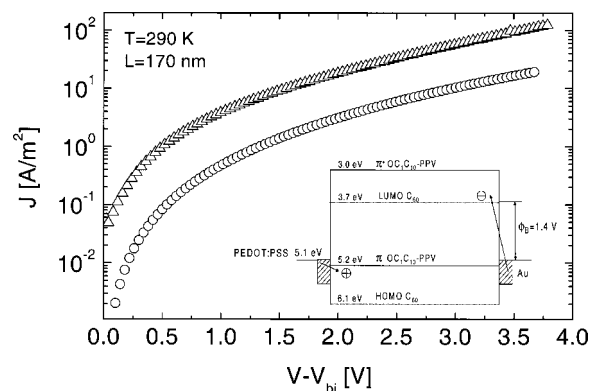


FIG. 2. The experimental  $J$ - $V$  characteristics of an ITO/PEDOT:PSS/PCBM/Au injection-limited electron current (triangles) and calculated space-charge limited hole current in OC<sub>1</sub>C<sub>10</sub>-PPV (circles) for thickness of  $L = 170$  nm and temperature  $T = 290$  K. The inserted figure represents the device band diagram under flat band condition of a bulk-heterojunction solar cell using Au as a top electrode.

under flatband condition. In forward bias, the hole injection into OC<sub>1</sub>C<sub>10</sub>-PPV from the ITO/PEDOT:PSS electrode gives rise to a space-charge limited current with a field and temperature dependence of the hole mobility. This bulk-limited hole current then competes with the injection-limited electron current from the Au into the PCBM. The relevant question is now whether the current in such a device is electron or hole dominated.

For this purpose the electron injection from Au into pure PCBM films has been studied. In Fig. 2, the experimental injection-limited electron current from a Au electrode into PCBM is plotted together with the calculated space-charge limited hole current in OC<sub>1</sub>C<sub>10</sub>-PPV for a thickness  $L = 170$  nm at a temperature  $T = 290$  K. Although the injection of electrons from a Au contact into PCBM is hindered by the presence of a large interface barrier due to the offset in energy levels, the injection-limited electron current in an ITO/PEDOT:PSS/PCBM/Au diode is still larger than the bulk space-charge limited hole current in the ITO/PEDOT:PSS/OC<sub>1</sub>C<sub>10</sub>-PPV /Au device. As a result, the approach of a Au-based hole-only device is not applicable to OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM bulk-heterojunction photodiodes. Apparently, the injection barrier of 1.4 eV (see Fig. 2) is not sufficient to suppress the electron current below the hole current, because  $\mu_e$  in PCBM is about a factor of 4000 larger than  $\mu_h$  in OC<sub>1</sub>C<sub>10</sub>-PPV.

In order to clarify the injection-limited electron current from Au into PCBM, its field and temperature dependence has been investigated. The classical models to treat charge injection into a dielectric are the Richardson-Schottky (RS) model of thermionic emission and the Fowler-Nordheim (FN) model for tunneling injection.<sup>7</sup> The tunneling from the contact (FN model) only becomes important at sufficient high fields due to the strong band bending. However, the classical RS model does not take into account the energy disorder, which is well known to control the transport in organic materials. It has been recently demonstrated<sup>8</sup> that the hole injection into OC<sub>1</sub>C<sub>10</sub>-PPV is consistently described by a hopping based model, which takes full account of both

positional and energetic disorder of the system and image force effect.<sup>9–11</sup> According to this model a charge carrier will make an initial jump from the Fermi level of the metal into localized states close to the metal–semiconductor interface, followed by either a diffusive escape from the interface or a backflow to the metal. A Monte Carlo simulation shows that the initial jump is essential and determines the temperature and field dependence of the injection process.<sup>9–11</sup> The injection-limited current density  $J$  (ILC) can then be analytically approximated by averaging the product of the frequency of the initial jumps of the charge carrier across the metal–polymer interface and the probability to escape recombination, over all site energies  $E$  and the initial jump distances  $x$ . Arkhipov *et al.* have shown that the ILC can be described by<sup>9–11</sup>

$$J = e \nu_0 \int_a^\infty dx \exp(-2\gamma x) w_{\text{esc}}(x) \int_{-\infty}^\infty dE \cdot \text{Bol}(E) g[U(x) - E], \quad (1)$$

where  $\nu_0$  is the attempt-to-jump frequency,  $a$  is the distance from the electrode to the first hopping site in the bulk, set to the average intersite spacing,  $\gamma$  is the inverse localization radius,  $w_{\text{esc}}$  is the probability for a carrier to avoid surface recombination,  $\text{Bol}(E)$  is the Boltzmann function for occupation statistics,  $g$  is the Gaussian density of states distribution, and  $U(x)$  is the electrostatic potential energy of the carrier. We note that in PCBM the electron transport states ( $E$ ) can be described by a Gaussian distribution, characterized by an energy width  $\sigma$  and nearest hopping distance  $a$ .<sup>5</sup> From the field and temperature dependence of the electron mobility of PCBM,  $\sigma = 0.073$  eV and  $a = (3.4 \pm 0.1)$  nm have been extracted.<sup>5</sup> The inverse localization radius equals  $\gamma = 10/\text{nm}$ .<sup>9</sup> The electrostatic potential  $U$  is represented by the sum of the barrier for charge injection, the image potential, and the external potential. As a result,  $U$  is subject to two material-dependent parameters, the dielectric constant  $\epsilon$  and  $\phi_b$ , the energy distance from the Fermi level of the electrode to the center of the Gaussian density of states of the PCBM transport states. Because the dielectric constant of  $\epsilon_r = 3.9$  has been found from impedance measurements,  $\phi_b$  is the only unknown parameter in Eq. (1).

In Fig. 3, the calculated ILC of PCBM according to Eq. (1) is plotted together with experimental data, for different temperatures. Using a barrier height  $\phi_b = 0.76$  eV (without any other free parameters), the calculated ILC is in a good agreement with experiment. Only at low fields the model calculations overestimate the experimental curves, the origin of this difference is subject of further investigations. Apparently, the injection barrier of the Au/PCBM contact is strongly reduced as compared to the band offset, from which a barrier of about 1.4 eV was expected. It has been demonstrated from ultraviolet photoemission spectroscopy that at the Au/C<sub>60</sub> a strong interface dipole exists, which lowers the Au/C<sub>60</sub> interface barrier with 0.64 eV.<sup>12</sup> Together with the band offset of 1.4 eV this would give rise to an injection barrier of 0.76 eV, which exactly equals the barrier as ex-

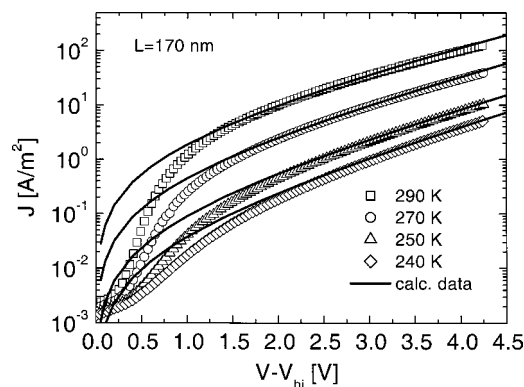


FIG. 3. Injection-limited electron current  $J$  vs voltage  $V$  as a function of temperature (symbols) for an ITO/PEDOT:PSS/PCBM/Au device with thickness  $L = 170$  nm. The calculated  $J - V$  characteristics [Eq. (1)] are plotted as solid lines. The estimated built-in voltage  $V_{\text{bi}} = 0.75$  V has been subtracted from the applied bias.

tracted from the  $J - V$  measurements. This interface dipole is then responsible for the relatively large injection-limited electron current of the Au/PCBM contact.

#### IV. CONCLUSION

$J - V$  measurements have demonstrated that the dark current in a OC<sub>1</sub>C<sub>10</sub>–PPV:PCBM (1:4 w/w) bulk-heterojunction photodiode is completely dominated by electron transport through PCBM. The electron mobility in the bulk heterojunction is identical to the electron mobility in pure PCBM. Even in devices where the injection of electrons is suppressed by a high work function Au contact, the injection-limited electron current into PCBM still exceeds the bulk hole current of OC<sub>1</sub>C<sub>10</sub>–PPV. The field and temperature dependence of this injection-limited electron current can be explained by a model based on thermally assisted hopping from the electrode into localized states of the PCBM.

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